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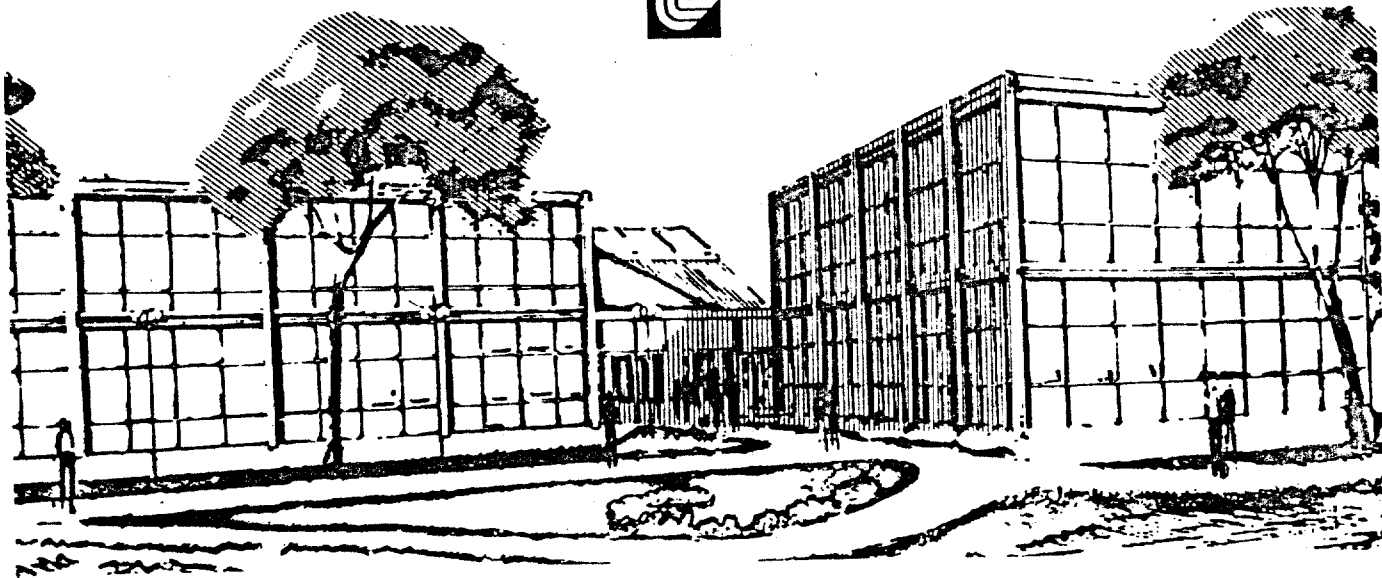
DEUTERIUM SEPARATION BY CO₂ LASER DISSOCIATION OF FLUOROMETHANES

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September, 1979

This paper was prepared for submission to CLEOS/ICF '80 in San Diego, California, February 26-28, 1980.

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DEUTERIUM SEPARATION BY CO₂ LASER DISSOCIATION
OF FLUOROMETHANES[†]

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ABSTRACT

Difluoromethane and trifluoromethane are the best candidate molecules for large-scale laser separation of deuterium. Absorption selectivity exceeds 1000 for both molecules. Dissociation with 2 nanosecond pulses permits high dissociation yield to 0.5 atmosphere with deuterium enrichment factors of 2000 for difluoromethane and 10,000 for trifluoromethane.

[†] Work performed under the auspices of the U. S. Department of Energy by the Lawrence Livermore Laboratory and Los Alamos Scientific Laboratory under contract number W-7405-ENG-48.

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SUMMARY

An extensive evaluation of candidate molecular systems suitable for large-scale laser separation of deuterium has resulted in the selection of only two near-optimum molecules--difluoromethane and trifluoromethane. Both molecules undergo deuterium-separation multiple-photon dissociation (MPD) following excitation by a CO₂ laser near 10.2-10.5 micron. Both satisfy the fundamental requirements for large-scale process viability, namely, greater than 1000-1 deuterium optical selectivity (σ_D/σ_H) in multiple-photon absorption, high dissociation yield near atmospheric pressure, and greater than 1000-fold single-step deuterium enrichment, β , in the dissociation products.

This paper presents the results of experiments in which β is measured in CHF₃ by carbon-isotope labelling of the reactants along with recent measurements of β and σ_D/σ_H in both molecules at high pressures (> 0.1 atm) using a short pulse CO₂ laser (FWHM ≈ 2 nsec).

It is difficult to measure the DF photoproduct of CDF₃ MPD (10.3 μ) directly in laboratory experiments due to the reactivity of DF with the walls of the reaction cell. However, the D/H ratio in the product (and therefore β) may be determined directly by irradiating a mixture of ¹²CDF₃/¹³CHF₃ and then measuring the ¹²C/¹³C ratio in the C₂F₄ product. Tetrafluoroethene is formed by recombination of CF₂ radicals which are produced in the nascent MPD step along with DF. In a pure ¹²CDF₃/¹³CHF₃ mixture there is a one-to-one correspondence between the formation of a

DF(HF) and the appearance of a $^{12}\text{C}(^{13}\text{C})$ in the C_2F_4 product; this is actually only approximately true in this experiment since because of the isotopic purity of the starting material is only 85% ^{13}C [$^{13}\text{CHF}_3$], but is easily taken into account. β was measured this way at a variety of wavelengths and other operating conditions using mixtures of 20 torr argon plus ~ 0.2 torr $^{13}\text{CHF}_3$, which was doped with about a 10^{-3} impurity of $^{12}\text{CDF}_3$. At 30 J/cm^2 fluence the CDF_3 dissociation probability is known to be nearly unity.⁽¹⁾ At this fluence β was found to be 2500 at 10.15μ , and increased rapidly toward longer wavelengths and was $> 20,000$ from 10.25 - 10.35μ . In addition, at 10.3μ , β was observed to decrease at higher fluences.

Very high (> 1000) values of the deuterium enrichment factor and absorption optical selectivity at > 0.1 atm pressure are necessary for industrially viable deuterium separation. In order to avoid collisional quenching of photoproduct yield, the sample must be irradiated by a short pulse CO_2 laser (FWHM ~ 2 nsec). The results of preliminary measurements of these quantities (performed at the Los Alamos Scientific Laboratory in collaboration with S. J. Thomas of LASL) have been previously reported⁽²⁾ by the authors. The results based on more refined analysis of this data are now presented for CDF_3 (R(26), 10.2μ) $\beta = 11,500^{+6500}_{-2500}$ at 100 torr for 30 J/cm^2 and $\sigma_{\text{D}}/\sigma_{\text{H}} = 1800$ at 2 J/cm^2 fluence, and CHDF_2 (P(14), 10.5μ): $\beta = 2500 \pm 200$ at 200 torr for 23 J/cm^2 and $\sigma_{\text{D}}/\sigma_{\text{H}} = 500$ at 2 J/cm^2 fluence.

Only by using ~ 2 nanosecond duration CO_2 laser pulses could high pressure operation be achieved. The photodissociation yield was near unity at 30 J/cm^2 for trifluoromethane and was found to be fairly independent of pressure up to 400 torr, beyond which yield fell slowly. Difluoromethane yield saturated near 29 J/cm^2 out to 400 torr, limited by breakdown within the gas. Additional results will be presented, along with their implication for photochemical production of heavy water.

REFERENCES

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- (2) J. B. Marling, I. P. Herman and S. J. Thomas, 1979 IEEE/OSA Conference on Laser Engineering and Applications, Presentation #4.2.

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